Paper No.
7801

NACE® INTERNATIONAL CORROSION 2016 CONFERENCE & EXPO

Experimental Studies to Determine Effects of Vapor Corrosion Inhibitors for Mitigating Corrosion in Casing

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ABSTRACT

Cased pipeline crossings are segments typically situated at road and railway crossings where the pipeline (carrier pipe) is surrounded by a larger diameter pipe (casing) for protection from mechanical damage. Although these locations face a similar threat of external corrosion as those which are conventionally buried; the management approach is considerably different. With time, spacers and end seals deteriorate and an environment conducive to external corrosion is created inside the casing leaving the pipeline vulnerable to damage if the coating system has also become compromised at any point. Execution of repair activities under these circumstances is very expensive and logistically challenging. Recently, a major North American pipeline operator has implemented gel-based vapor corrosion inhibitors (VCIs), in conjunction with cathodic protection to contend with such situations and control external corrosion of the carrier pipe at cased crossings. A VCI fluid mixture is initially injected into the casing's annular space at a water equivalent viscosity and within a designed period of time it sets to a gel-like consistency. Since the gel is electrically conductive, it enables the carrier pipe to also receive cathodic current. Although the technique is proving to be very effective based from pipe-to-soil potential and ER probe measurements perspectives; some debate exists within industry regarding the simultaneous application of the two mitigation practices. This paper presents compatibility testing of VCI gel and CP and discusses the influences, effects or interactions between the two corrosion control methodologies. The overall objective of the project is to comprehensively identify and understand any offsetting effects between the concurrent use of VCI gel and cathodic protection inside a casing. The paper details results of laboratory experiments on VCIs for mitigating corrosion of casings.

Keywords: vapor corrosion inhibitor, cased crossing, and cathodic protection

VCI A is Cortec Corrologic Casing Filler
VCI B is product of Zerust/NTIC

INTRODUCTION

Onshore oil and gas pipelines routings often must pass beneath other critical infrastructure, such as highways, railroads, and waterways. Many North American operating pipelines were constructed over 50 years ago therefore corrosion prevention and related repairs are becoming more prevalent to avoid dangerous and costly releases. Ironically, pipeline segments that lie beneath some of the most sensitive areas are also among the most difficult to inspect[1,2] and therefore require attention. Cased pipelines are subject to not only the normal corrosion caused by time, moisture, and soil chemistry, but also galvanic corrosion caused by contact between the metals of the carrier pipe and its casing.[3] Furthermore, the outer casings can adversely affect cathodic protection systems installed to reduce corrosion if there is metallic contact between the casing and the carrier pipe.

Cased pipeline crossings are segments typically situated at road and railway crossings where the pipeline (carrier pipe) is surrounded by a larger diameter pipe (casing) for protection from mechanical damage. Although these locations face a similar threat of external corrosion as those which are conventionally buried; the management approach is considerably different. Cased pipelines often are sealed or have a separating medium such as wax placed between the layers of pipe. With time, spacers and end seals may deteriorate and an environment conducive to external corrosion is created inside the casing leaving the pipeline vulnerable to damage if the coating system has also become compromised.[4] Furthermore, the spacers that separate the carrier and casing pipe can break down over time, creating metallic contact between the carrier and casing pipes. It is estimated that there are close to 1 million cased-crossings in the U.S., with a high percentage having degraded to the point of metallic contact between the casing and pipe. Execution of repair activities under these circumstances is very expensive and logistically challenging. External, visual inspection of cased pipelines is often impractical because of their location. Some are inaccessible, and in other cases obtaining a permit to perform an inspection dig may be difficult or impractical. Inspection of a cased pipe segment requires uncovering the segment, opening the space between pipe layers, and inserting an instrumented probe between layers to inspect the inner pipe's integrity. Internal inspection by sending a tubular, instrumented device known as a "pig" through the carrier pipeline along with the product requires no excavation, but it is expensive and usually is done every five years.

Recently, a major North American pipeline operator has implemented gel based vapor corrosion inhibitors (VCIs), in conjunction with cathodic protection control external corrosion at cased crossings.[4] A VCI fluid mixture is initially injected into the casing's annular space at a water equivalent viscosity and within a designed period of time it sets to a gel-like consistency. Since the gel is electrically conductive, it enables the carrier pipe to receive cathodic current. Although the technique is proving to be very effective based from pipe-to-soil potential and ER probe measurement perspectives; some debate exists within industry regarding the parallel application of the two mitigation practices. The compatibility testing of VCI gel and CP that is being conducted will determine any influences, effects or interactions between the two corrosion control methodologies. The study will also determine whether CP current can be partially diverted to the casing from the carrier pipe within the gel filled environment. Results from this effort will be compiled to further validate and optimize the use of VCI gel for this application. The overall objective of the project is to comprehensively identify and understand any offsetting effects between the concurrent use of VCI gel and cathodic protection inside a casing. The paper documents the experimental effort of this project. Specifically, this paper documents various electrochemical properties of the two VCIs, and their effects on corrosion mitigation of the casings.

EXPERIMENTAL

Two VCIs were tested from two major independent corrosion inhibitor suppliers. The VCIs are identified as VCI "A" and VCI "B". Two corrosion cells were setup to test each of the VCIs. Each corrosion cell was setup using the three-electrode configuration: (i) a working electrode, (ii) a counter electrode made of platinum-coated niobium wire mesh, and (iii) a saturated calomel reference electrode. The working electrode for the each corrosion cell was prepared using 1-ft (30.5cm) long and 2.375 (60mm) inch diameter API[1] 5L X52 grade carbon steel pipe. One end of the each pipe was sealed to avoid ingress of electrolyte inside the pipe. Only the exterior surface of the pipe was exposed to the electrolyte in each corrosion cell. Images of the two working electrodes are presented in Figure 1.

(a) VCI A Working Electrode **(b) VCI B Working Electrode**

Figure 1. (a) VCI A and (b) VCI B Working Electrodes

A Pt-coated niobium mesh was used as the counter electrode. The mesh specifications are following. Diameter of each wire in the mesh was 0.508 mm (20mils) with Pt thickness of 2.54 µm (0.1mil). The mesh pattern was 10 × 10 wires/inch^2 (approximately 4X4 wires/cm^2) with an active surface area of 1.25 in^2/in^2 (cm^2/cm^2). An image of the counter electrode assembly along with its placement in the corrosion cell is shown in Figure 2. Saturated calomel electrode was used as the reference electrode for each corrosion cell. The reference electrode was brought in contact with the cell electrolyte using the luggin probe.

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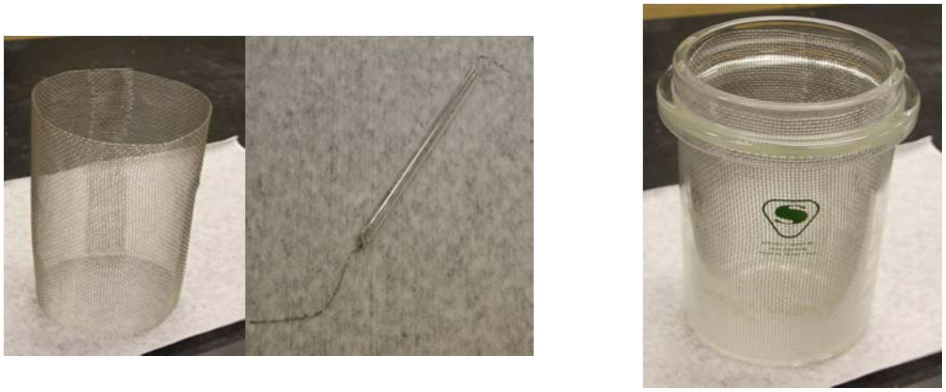
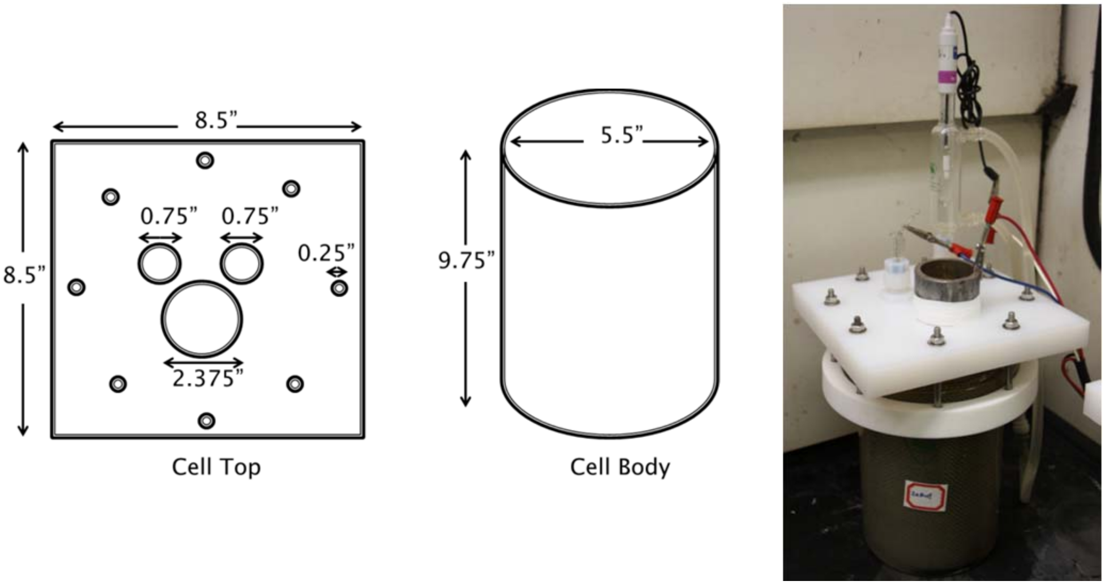


(a) Counter Electrode Assembly **(b) Counter Electrode Inside the Cell**

Figure 2. (a) Counter Electrode Assemble, (b) Counter Electrode Inside the Corrosion Cell



(a) Cell Schematic **(b) Assembled Cell**

Figure 3. Corrosion Cell Used to Conduct the Various Electrochemical Tests on the Gel Sample

The electrolytes for the corrosion cell were prepared according to the VCI mixing formulas provided by the vendors. The tap water was used as the mixing media for the VCIs which consisted of vapor phase inhibitors and gelling materials. Approximately 0.6 gallons (2.3 L) of the electrolyte was prepared for each corrosion cell. A schematic of the corrosion cell and an image of one of the assembled corrosion cell is presented in Figure 3.

The cell was connected to a potentiostat plus frequency response analyzer (VMP3[†] model) controlled by EC-Lab[†] software. The working, counter, and reference electrodes were interfaced with a potentiostat plus frequency response analyzer. Various electrochemical tests were carried out including open circuit potential measurements, electrochemical impedance spectroscopy, potentiodynamic and potentiostatic polarization measurements.

EXPERIMENTAL DATA AND RESULTS

The open circuit potential of the working electrode with respect to the saturated calomel electrode (SCE) is plotted in Figure 4. As seen in Figure 4, the open circuit potential reach the steady state after approximately 50 hours for VCI A, and 160 hours for VCI B. This indicated that it takes approximately 2 days for the pipe material to equilibrate with VCI A, and 7 days for VCI B. The corrosion potentials for the pipe material in VCI A and B are approximately -0.028 and -0.044 V_{SCE}, respectively.

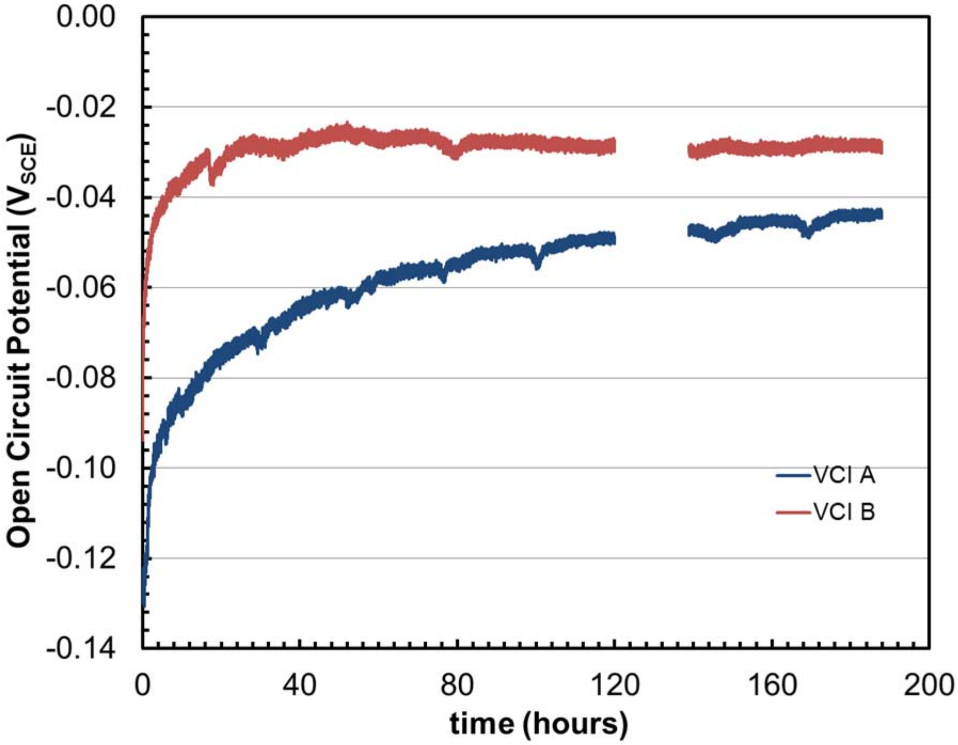
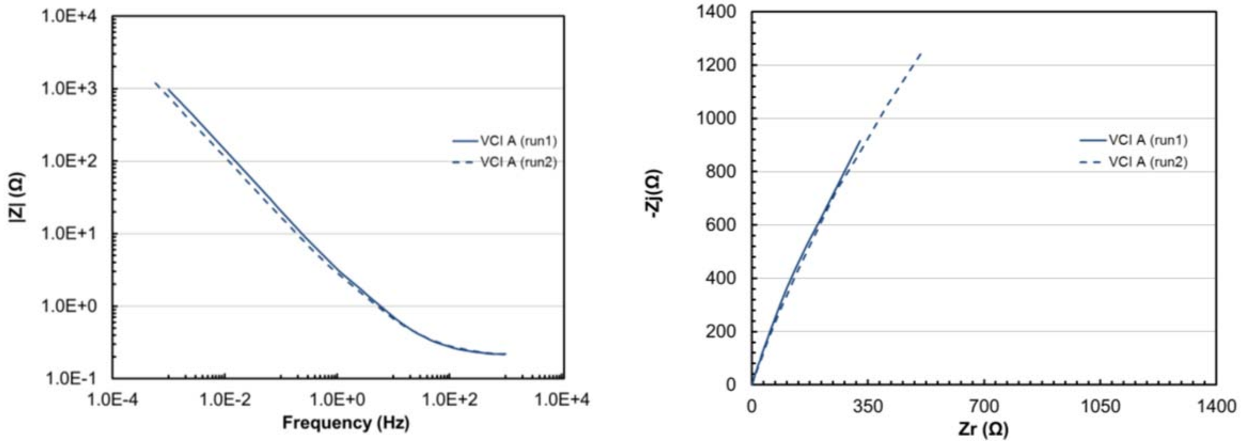


Figure 4. Open Circuit Potential Versus Time

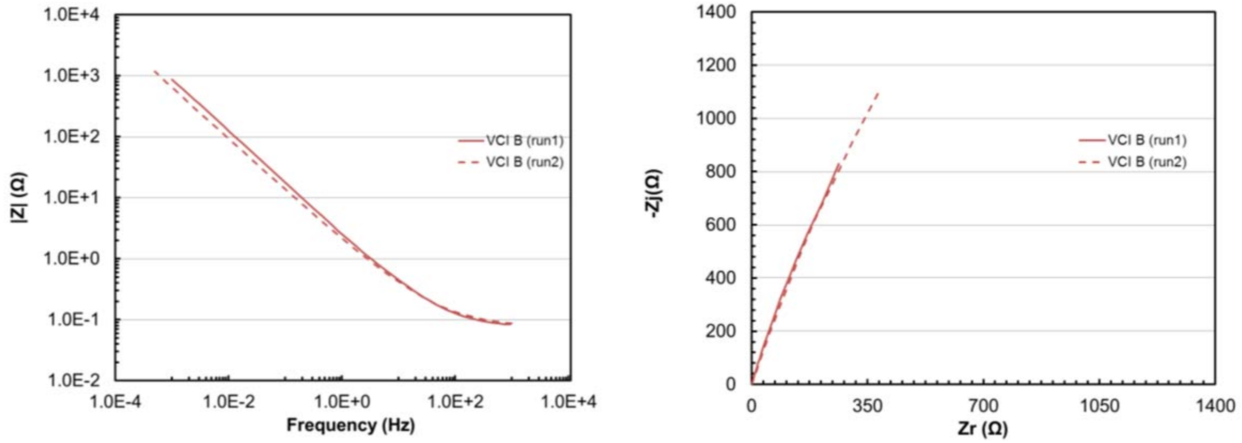
After the corrosion potentials of the working electrodes stabilized in the corrosion cells, electrochemical impedance spectroscopy (EIS) was used to measure several impedance spectra of the working electrode in each corrosion cell. Two EIS measurements were conducted per cell. All of the EIS measurements were conducted at the open circuit potential of the corrosion cell and the data were used to estimate the polarization resistance. The Nyquist and Bode plots of the impedance spectrum are presented in Figures 5(a) and (b) for VCI A. Similarly, the Nyquist and Bode plots of the impedance spectrum are presented in Figures 5(c) and (d) for VCI B.

[†] Trade name.

An electrical circuit was used to fit to the impedance data shown in Figures 5(a) to 5(d). The equivalent circuit is shown in Figure 6. The equivalent circuit consists of a constant phase element in parallel with the polarization resistance, and both in series with a solution resistance. In the equivalent circuit, Rp and Cdl represent the polarization resistance and capacitance at the electrode surface, and α is used to model non-ideal capacitive behavior of the electrode surface. A comparison of the equivalent circuit fit to the impedance data for the four spectra is presented in Figure 7. As seen in the figure, the equivalent circuit provided a good fit to the impedance data collected from the four runs.



(a) VCI A, Bode Plot **(b) VCI A, Nyquist Plot**



(c) VCI B, Bode Plot **(d) VCI B, Nyquist Plot**

Figure 5. Nyquist and Bode Plots of the Impedance Spectrum for VCI A and VCI B

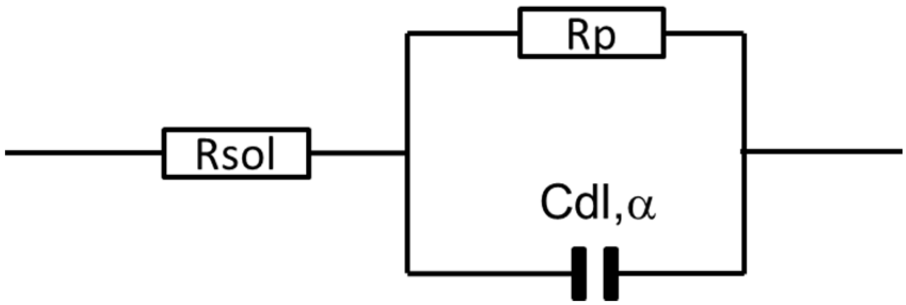
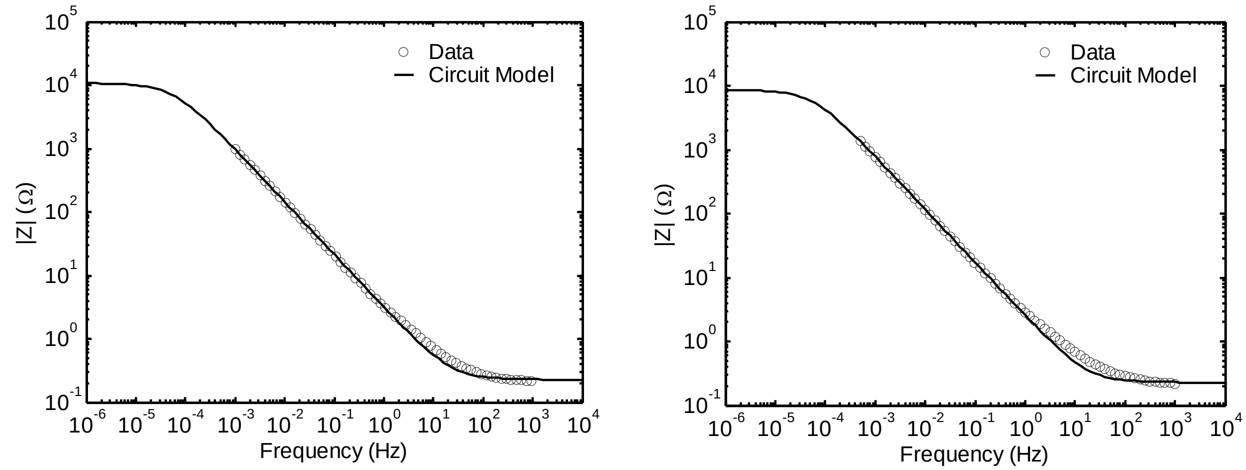
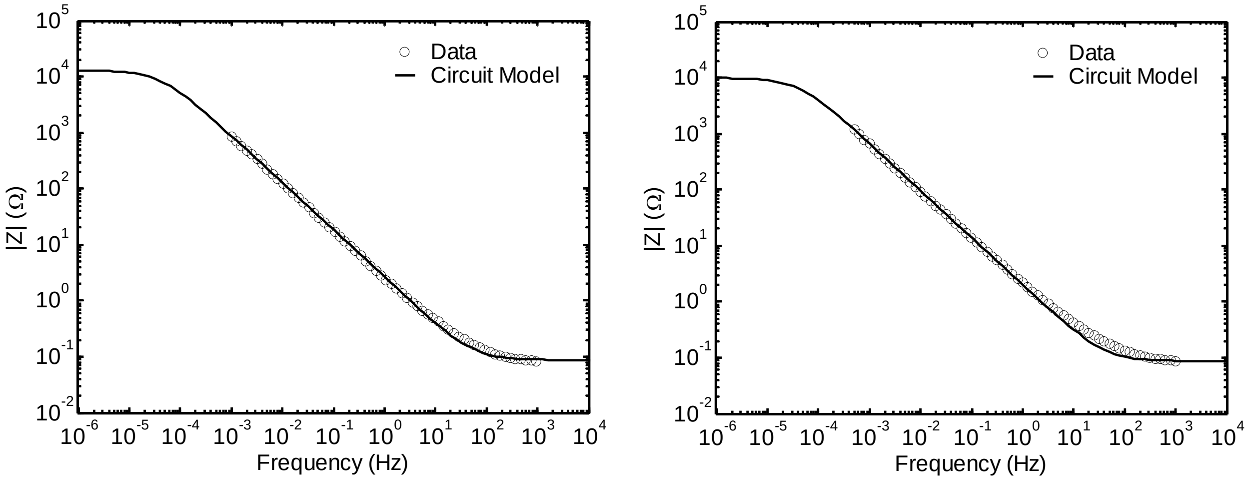


Figure 6. Circuit Model Used to Fit the Impedance Data



(a) VCI A, Run 1 **(b) VCI A, Run 2**



(c) VCI B, Run 1 **(d) VCI B, Run 2**

Figure 7. Comparison of the Circuit Model Fit to the Electrochemical Impedance Spectroscopy Data in Figure 5

The corrosion rate of the working electrode was estimated using the polarization resistance (Rp) values obtained by fitting the equivalent circuit model to the ESI data. The estimated Rp values were normalized with respect to the surface area of the electrode by multiplying the polarization resistance values with the electrode surface area of $60in^2$ ($385.1\ cm^2$). The normalized polarization resistance was used to obtain the corrosion current density (i_{corr}) according to the Stern-Geary equation (1957)[5]:

$$i_{corr} = 10^6 \times B/\ R_{pa} \tag{1}$$

Where:

i_{corr} — corrosion current density [$\mu A/cm^2$]
R_{pa} — normalized polarization resistance [$\Omega\text{-}cm^2$]
B — composite Tafel parameter [V]

B is defined as (ASTM International, 2010)[6]

$$B = \beta_a \beta_c / [2.303(\beta_a + \beta_c)] \tag{2}$$

Where:

β_a — anodic Tafel slope [mV/decade]
β_c — cathodic Tafel slope [mV/decade]

Values of β_a and β_c were obtained from the anodic and cathodic polarization curves collected after the EIS measurements. The polarization curves were collected with the scan rate of 2 mV/sec. This scan rate is approximately 10 times higher than recommended for the linear polarization resistance method. It was necessary to use the higher scan rate to achieve high signal to noise ratio. The polarization curves are presented in Figure 8. Two polarization curves were collected for each VCI. In the first polarization curve for each VCI, a Tafel region with very large values of anodic and cathodic Tafel slopes were observed [see Figures 8(a) and 8(c)]. Therefore, a second polarization curve (denoted as Run 2 in Figure 8) for each VCI was measured. The Tafel region in the second polarization curves was well defined for both the VCIs. This data was used to estimate β_a and β_c in Eq. (2). The estimated values of β_a and β_c are approximately 470 and 250 mV/decade, respectively, for both VCI A and VCI B. The computed value of B is 71 mV.

The corrosion rates were calculated using the following equation (ASTM International, 2010):

$$CR\left(\frac{mm}{yr}\right) = 3.27 \times 10^{-3}\,\frac{EW\ i_{corr}}{\rho} \qquad (3)$$

Where:

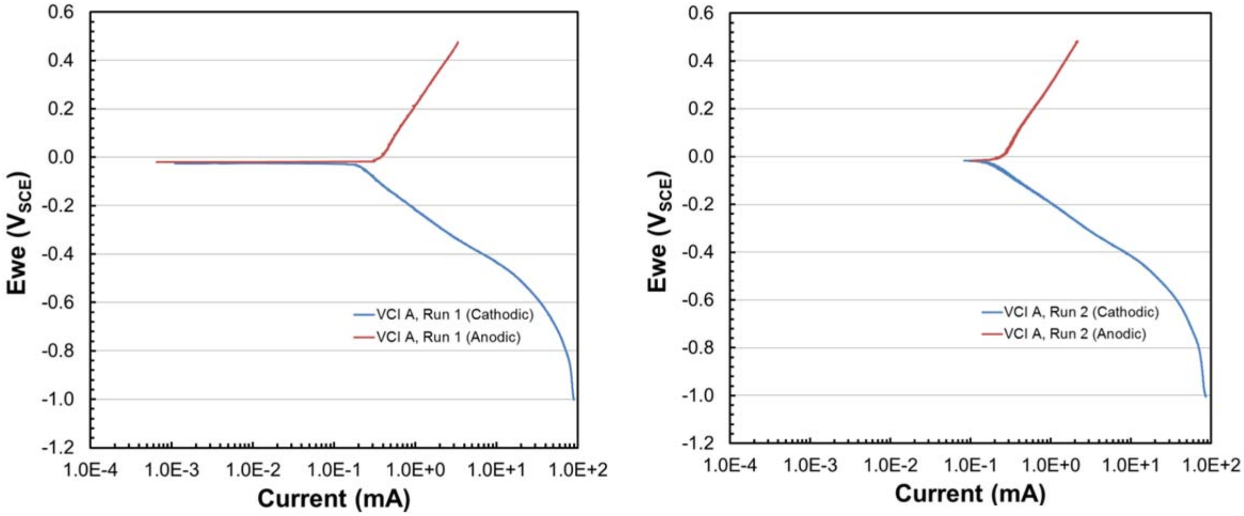
EW — equivalent weight of carbon steel [g] = 27.92 (ASTM International, 2010)
ρ — density of carbon steel [g/cm^3] = 7.86 (ASTM International, 2010)

The polarization resistance values obtained from the equivalent circuit fits to the experimental data listed in Table 1. The normalized polarization resistance values were input in Eq. (1) along with the value of *B* to calculate i_{corr} for each value of R_{pa}. Following this, the corrosion rates were calculated using Eq. (3). The calculated corrosion rates were multiplied by a factor of 1000/25.4 to convert to units of mils/yr. The calculated corrosion rates are listed in Table 1.

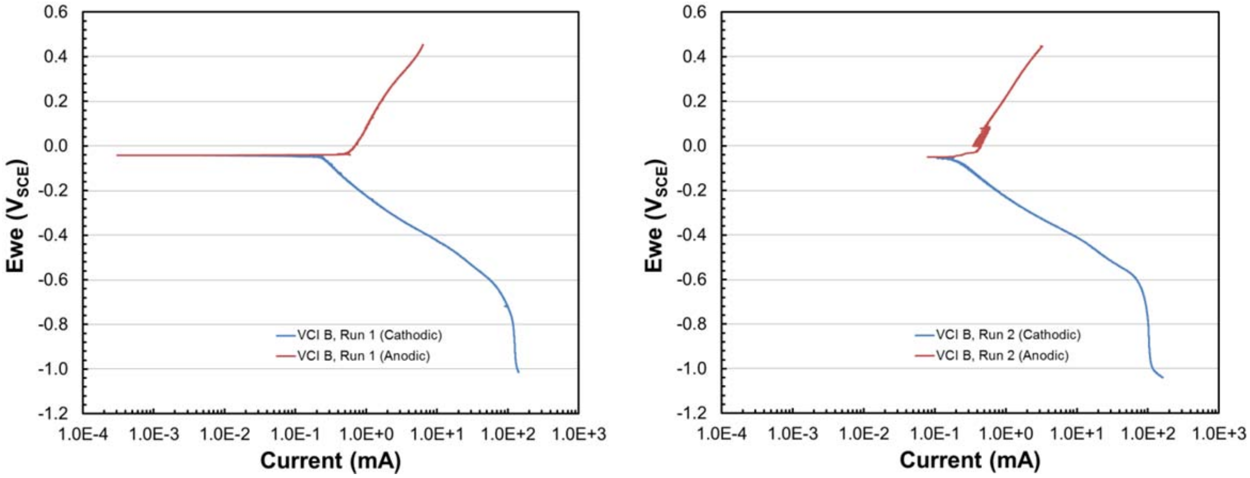
Table 1. Polarization Resistance Values Estimated From the Circuit Model Fit to the Impedance Data and Calculated Corrosion Rate of the Electrode

Impedance Spectrum	Polarization Resistance (Ohm)	Corrosion Rate mils/yr
VCI A, Run 1	10805.1	7.8×10^{-3}
VCI A, Run 2	8689.2	9.7×10^{-3}
VCI B, Run 1	13037.0	6.5×10^{-3}
VCI B, Run 2	9990.0	8.4×10^{-3}

To determine the response of the working electrode under cathodic polarization, potentiostatic polarization curves were collected at three levels of the cathodic polarization for both VCIs. The working electrodes in the both the corrosion cells were potentiostatically polarized at a certain potential for approximately 120 hours. The current between the working and counter electrode was measured. The polarization curves for VCI A are presented in Figure 9.



(a) VCI A, Run 1 **(b) VCI A, Run 2**



(c) VCI B, Run 1 **(d) VCI B, Run 2**

Figure 8. Anodic and Cathodic Polarization Curves for the Electrode in VCI A and VCI B Corrosion Cells. Two Repeat Runs Were Collected in Each Cell.

The current versus time curves in Figure 9 are at -675, -775, and -875 mV$_{SCE}$ polarization levels. These potential values are equivalent to -750, -855, and -950 mV with respect to the Cu/CuSO$_4$ reference electrode. As seen in Figure 9, the current reach steady state in approximately 24 hours after polarizing the electrode. In addition, the steady state current is cathodic (i.e., negative) for the three levels of the polarization. This indicates that dominant electrochemical reaction at the electrode surface is reduction of certain chemical species. For -675 mV$_{SCE}$ polarization level, a small amount of oxidizing current is noted immediately after applying the polarization. However, the oxidizing current subsides within eight hours. Further, the magnitude of the oxidizing current is less than 0.4 mA.

The current versus time curves for VCI B are presented in Figure 10. The curves in Figure 10 are at -675, -775, and -875 mV_{SCE} polarization levels. For -675 mV_{SCE} polarization level, a large amount of oxidizing current is noted immediately after polarizing the working electrode. The cell was temporarily disconnected for few minutes at 4 hours after starting the experiment.
This action appears as discontinuity in Figure 10 for the -675 mV_{SCE} polarization level. The current eventually stabilized and reached a steady state at cathodic level. No such anomalies were observed for the -775 and -875 mV_{SCE} polarization levels.

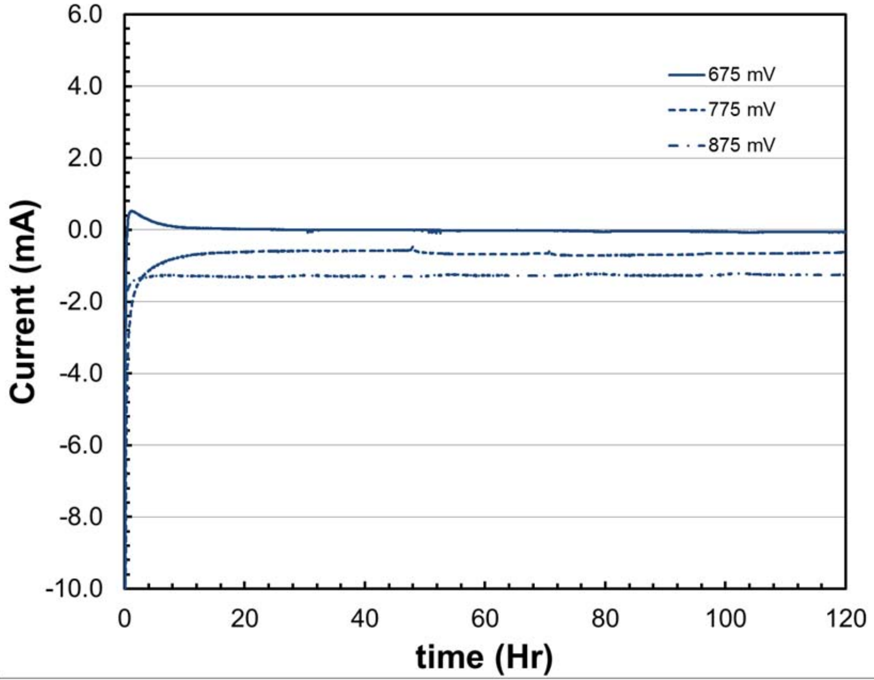


Figure 9. Potentiostatic Polarization Curves for VCI A

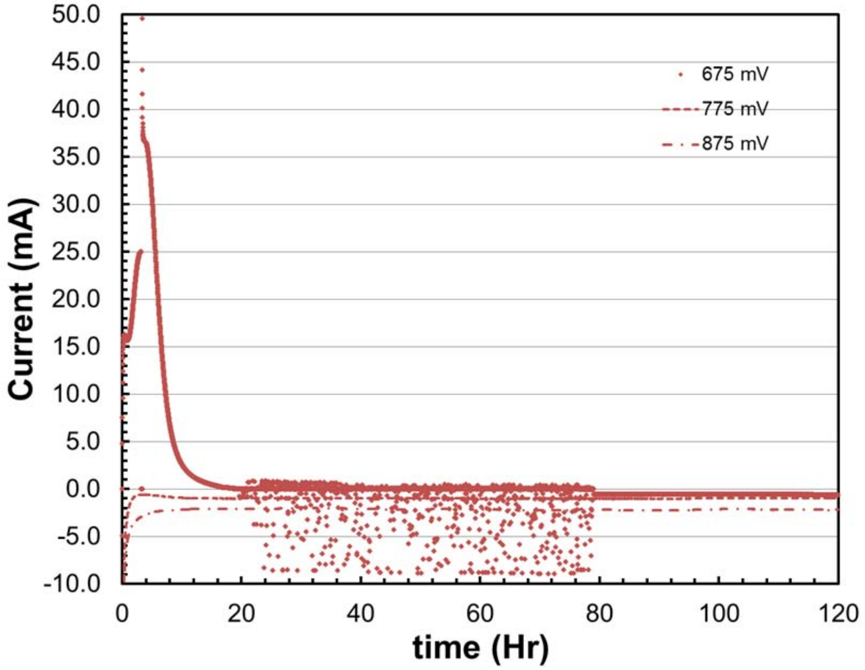


Figure 10. Potentiostatic Polarization Curves for VCI B

The steady-state current and current densities for the three polarization levels are listed in Table 2. The current density was obtained by normalizing the current value with the surface area of 60in^2 (385.1 cm^2)

Table 2. Steady-State Current and Current Density for Various Polarization Levels

Polarization Level (mV$_{SCE}$)	VCI A		VCI B	
	Current (mA)	Current Density (mA/m^2)	Current (mA)	Current Density (mA/m^2)
-675	-0.06	-1.6	-0.63	-16.4
-775	-0.69	-11.8	-0.98	-25.4
-875	-1.25	-32.3	-2.16	-56.1

The current densities listed in Table 2 are compared to the NACE recommended current density required to protect steel structures buried underground. As per the specification in NACE International (2002)[7], approximately 10–20 mA/m^2 are recommended to protect a holiday on a pipeline buried underground with soil resistivity of 0.5–5 Ω-m, and 20 mA/m^2 (2mA/ft^2) are recommended for soil resistivity of 0.5 Ω-m. Similarly, only 1-10 mA/m^2 (0.1-1.0 mA/ft^2) is recommended to protect the holiday in soil with a resistivity range of 5–15 Ω-m. A comparison of the values listed in Table 2 and the NACE recommended values indicate that higher CP supplied current density is needed to achieve the polarization level for satisfying the 850 mV off-potential criterion.[8]

SUMMARY

Experimental studies were conducted to determine the effects of VCIs on mitigating corrosion of cased pipeline sections. Two commercially available VCIs were tested using various electrochemical methods. The corrosion rate of API 5L X52 grade carbon steel is less than 0.01 mpy (0.25 µm) for the two commercially available VCIs. The measured corrosion rates indicate that VCIs are effective in mitigation corrosion of the carrier pipe in the cased pipeline section. The experimental data also indicate that cathodic current densities with VCIs are somewhat higher than for a holiday in contact with soil. This suggests that more CP current would be needed to meet the 850 mV off-potential criterion with the application of the VCI gel in casing annuli.

ACKNOWLEDGMENT

The authors would like to recognize and sincerely thank Enbridge Pipelines' Mike Hill, Yvan Hubert, Kurt Baraniecki and Walter Kresic for their continual support, dedication and devotion towards advancing pipeline integrity management.

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